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Patents ADP number *(if you know it)* 4001590001

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United Kingdom

4. Title of the invention

EXTRACTION OF METAL SALTS

5. Name of your agent *(if you have one)*

J.Y. & G.W. JOHNSON

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Number of earlier application	Date of filing *(day / month / year)*

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Claim(s)	3
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R.T. MANATON
0171 405 0356

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DUPLICATE

EXTRACTION OF METAL SALTS

This invention relates to the extraction of metal salts from aqueous solutions. More specifically it relates to methods for extracting metal cations and their associated anions which avoid returning any ionic species to the solution, thus leaving the acidity of the solution unchanged and purifying it by de-ionisation. Methods according to the invention are of use particularly (though not exclusively) in waste remediation and in the recovery of metals from primary sources.

Two main methods are currently used for the extraction of metallic ions from solution. Both involve the use of an extractant reagent: in the first method this is mixed with the solution from which the metal ions are to be removed ("solvent extraction"), and in the second it is immobilised on a solid support.

Current solvent extraction technology is based on the reaction scheme shown schematically in Figure 1. In this system an acidic extractant is used to remove a metal cation from an aqueous feed stream. The metal n^+ cation is replaced by n protons and the anion is left in the solution. The overall effect on the feed stream is to replace a metal salt MX with a mineral acid H_nX and this leads to an increase in the acidity of the aqueous feed stream.

This type of reaction is widely used for the extraction of copper from oxidic ores, the acid introduced into the stream reacting with insoluble metal oxides to give soluble metal salts. Indeed, this reaction scheme is particularly suited to the extraction of metals from metal oxides since the overall reaction has a perfect mass balance equation:

$$MO + Power = M + \tfrac{1}{2}O_2$$

However, this extraction technique suffers from a number of shortcomings. For instance, it is not suitable

for use in relation to feed streams which have a very hi[redacted] metal tenor (i.e. a high concentration of metal in t[redacted] feed), since removal of metal ions rapidly decreases the pH of the solution, and this renders the extractant ineffective. A similar effect is observed if the feed stream itself has a low pH value. For the same reason, if acid is not consumed in the leach process, pH will decrease and the extractant will become ineffective unless action is taken to neutralise the stream. This is particularly important in oxidative pressure leaching of sulfidic metal ores and biological leaching of sulfidic ores, where oxygen or oxygen and microbes are used to convert sulfides into sulfates without consumption of acid. Furthermore, the waste water from such extraction techniques cannot be discharged to the environment after metal extraction since, again, neutralisation of the acid would be required prior to discharge.

As far as solid supported reagents are concerned, most of these operate as ion exchange materials. The reagent on the solid phase support binds a metal cation and releases a cation (usually Na^+ or a proton) to the aqueous phase. Thus, the metal ion in solution is replaced either by sodium ions which increases the salinity of the solution, or by protons which reduce the pH of the feed solution. In either case the anion is left in solution.

We have now found that it is possible, through careful engineering of the ligand, to extract metal cations from a solution and simultaneously to extract their associated anions. This method has the advantage that the whole metal salt is removed from the feed stream, the pH of the stream is unaltered, and no additional species are added to the feed stream.

The ligands of use in the method of the invention have binding sites for both cations and anions, in contrast to the vast majority of existing ligands which bind only cations. The invention therefore provides, in one aspect,

a method of removing both the cation(s) and the anion(s) of a metal salt from an aqueous medium, by means of a ligand having binding sites for both the cation(s) an anion(s).

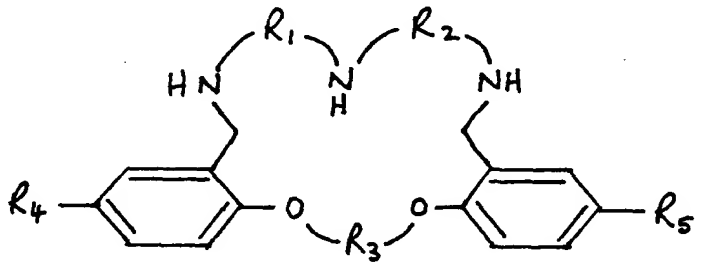
The method of the invention may either be carried out as a solvent extraction process of by use of a solid phase ligand. In the solvent extraction process, the ligand preferably has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, which may readily be achieved by judicious choice of side chains to render the ligand substantially hydrophobic. Preferably, the method involves the steps of adding the water-immiscible extraction medium to the aqueous medium (whereby the ligand with the cation(s) and anion(s) bound thereto is partitioned preferentially a water-immiscible phase), and separating the water-immiscible phase with the cation(s) and anion(s) therein from the aqueous phase.

For operation as a solid-phase extractant, the ligand may simply be immobilised on a solid support. By contacting the support-bound ligand with the aqueous feed stream, the metal salt may thereby be removed in a simple one-step process, without the need for a separation step. A solid-phase extraction is particularly useful for sequestering species from dilute solutions, in respect of which solvent extraction tends to be cumbersome and inefficient. The method will be particularly useful in the remediation of contaminated streams, especially those which are acidic, for example in the removal of actinide salts produced in the nuclear industry.

In both solvent and solid based methods, metal cations and their associated anions removed from the solution simultaneously, and no species are returned to the feed stream in their place. This makes the processes suitable for use in many applications for which the prior art methods are unsuitable, since the pH of the feed stream is unaltered, the feed stream is purified by de-ionisation, and, within limits that will be defined by the specific

reagent used in the process, metal cations and anions can be extracted at low pH without further lowering the pH. For the sake of simplicity and clarity the invention will hereafter be described principally with respect to solvent extraction processes, but the skilled man will have no difficulty in adapting the techniques for use in analogues solid-phase systems.

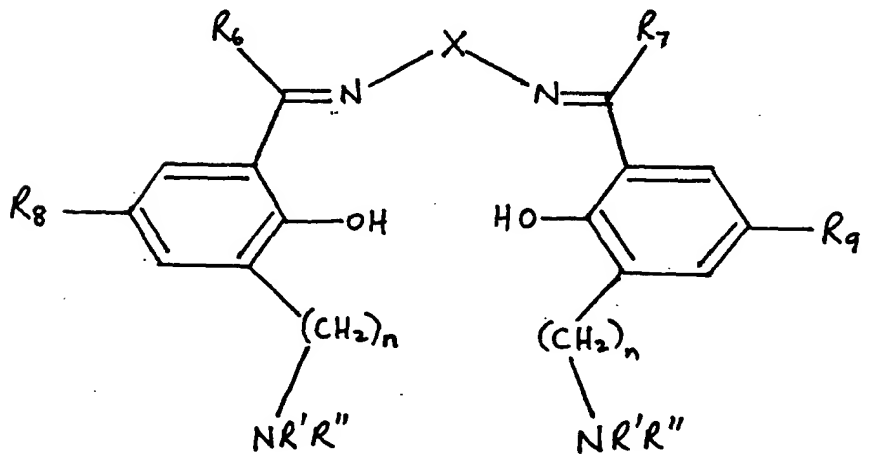
The applicants have developed two distinct classes of ligand for use in the processes of the invention. The first class ("Type I") have the following general formula:



where: R_1, R_2 and R_3 are, independently, optionally substituted C_2 to C_4 linkages;

R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

The second class ("Type II") have the formula:



where: X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n = 2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

NR'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring.

In both cases the side chains (R_4, R_5, R_6, R_7, R_8 and R_9) do not take part in ligand binding, and may be freely chosen with reference to the nature of the extraction medium in order to afford maximum solubility of the ligand therein. Hydrocarbon extraction media are preferred, and thus the side chains will normally confer hydrophobicity.

In the Type II ligands, it is believed that the metal cation binds first to the nitrogen atoms of the C=N groups and to the phenolic oxygen atoms. The phenolic protons are then displaced and protonate the nitrogen atoms of the tertiary amine groups, producing a positively charged binding site for the anion. The precise binding mechanism for the Type II ligands has yet to be elucidated.

Use of either class of ligand is effective to remove both the cations and anions of a metal salt from the feed stream. When decontamination of the feed stream is the sole aim, removal of the metal salt may be regarded as an end in itself. In most cases however, it is desired to extract the cations as elemental metal, and indeed this is the primary aim of ore extraction methods. A major advantage of the method of the invention is that the anion may also retrieved; for instance the anion (such as sulphate) may be

precipitated as an ammonium salt, which may then be used as a fertiliser.

The method of cation and anion precipitation depends on the class of ligand. For Type I ligands, contact with an aqueous ammoniacal solution liberates an ammoniacal solution of the metal salt from which the metal can be electrolysed. The electrolysis step produces metal and acid. Continual addition of ammonia to the system is required to neutralise the acid produced, and a by product of the reaction is an ammonium salt. For Type II ligands, the metal cation may also be recovered by contacting with strong acid. The metal cation M^{n+} in the hydrocarbon solution is replaced by n protons generating the 'acid' form of the reagent LH_nX. This allows electrolysis of the metal from an acidic medium. The resulting solution is then contacted with ammonia solution, regenerating the reagent L and producing an ammonium salt as a by product.

In each case the overall reaction is the same, and may be represented by the reaction scheme illustrated in Figure 2. The overall mass balance for this system is:

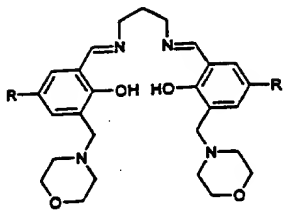
$$MS + 1\frac{1}{2}O_2 + H_2O + 2NH_3 + Power = M + (NH_4)_2SO_4$$

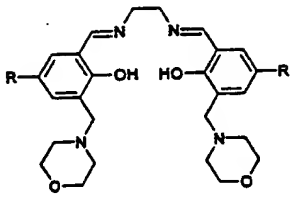
In a waste remediation application, for example removal of metal salts from acid mine drainage streams, the reaction scheme is illustrated in Figure 3; the overall mass balance is:

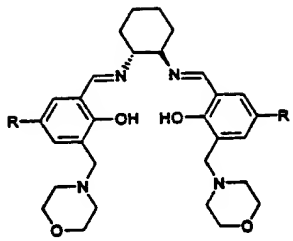
$$MSO_4 + H_2O + 2NH_3 + Power = M + (NH_4)_2SO_4 + \frac{1}{2}O_2$$

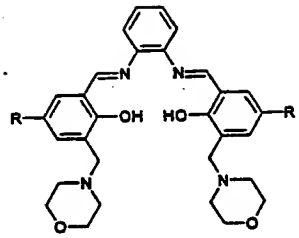
The Type I ligands are known in the literature, though not for the purpose of removing metal salts from aqueous solutions as in the present invention; their synthesis will therefore not be described herein. The present invention is accordingly described hereinafter in more detail with

eference to the synthesis and activity of various ligands of the Type II formula, in particular as follows:



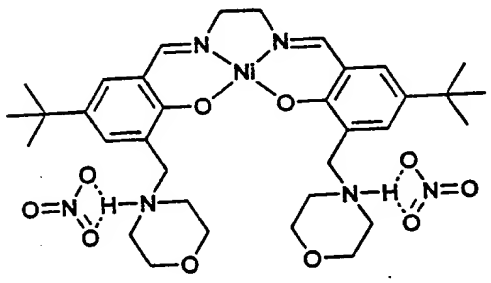


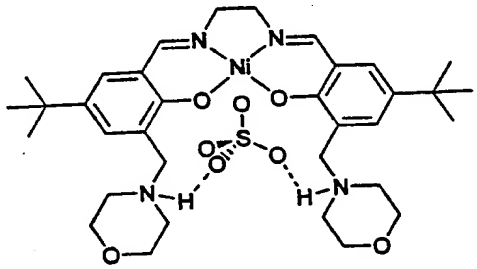




Me	**4**	**5**	**6**	**7**
tBu	**8**	**9**	**10**	**11**
Nonyl	**12**	**13**	**14**	**15**

By way of example, X-ray structure studies have demonstrated that the mode of binding of nickel nitrate and nickel sulfate to ligand number 9 is generally as shown below. As will be seen, the protons liberated from the phenolic groups in the metal binding site remain incorporated in the ligand, and protonate the basic pendant morpholine groups to form the anion binding site(s).



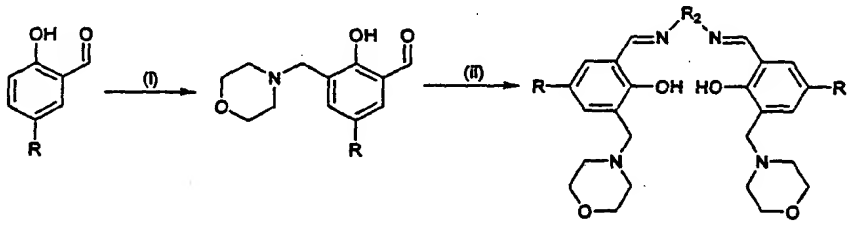


Solvent extraction studies have been used to characterise the extraction behaviour of these ligands, a are summarised in the Table below:

Feed pH	% Ni extracted	% S extracted
1	0	100
3	60	100
5	100	?
7	100	0

In order for the extraction system to be viable a plateau pH range must exist at which both nickel and sulphur are extracted with 100% efficiency. This can be engineered into the molecule by judicious choice of chelating moiety and internal base.

The ligands may be produced according to the following general reaction scheme, which is based on Schiff base type SALEN chemistry:



The invention will now be exemplified by reference to the following experimental results relating to the synthesis of various ligands, and their use in chelating various metal salts.

Synthesis **– N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine.**

5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde (6.000g, 21.7 mmol) was dissolved in diethyl ether (60ml) and poured into a solution of ethylene diamine (0.636g, 10.6mmol) in ethanol (60ml). The resulting yellow solution was stirred overnight and concentrated in vacuo to give crude product as a yellow oil. This was triturated in hexane at –78°C (CO_2/acetone) to give a waxy yellow solid, which was washed with hexane (15ml) and ether (15ml) and dried in vacuo. MP 155-158 °C. Calculated for $C_{34}H_{50}N_4O_4$ – 70.56%C, 8.71%H, 9.68%N, found 70.60%C, 9.06%H, 9.67%N. FAB-MS m/z, normalised intensity, [assignment]: 579, 62.1% [MH^+]; 578, 49.2%, [M^+]; 491,19.4%, [M^+ - morph]; 407,76%, [MH^+ - 2 morph]; 349, 11.9%, [M^+ -2 morph – ^tBu]. Where morph = $O(CH_2CH_2)_2N^+$, ^tBu = $(CH_3)_3C^+$. NMR ($CDCl_3$) ^1H: δ 1.28 (s, 9H, ^tBu), 2.50 (t, J=4.6, 4H, morpholinyl), 3.58 (s, 2H, benzylic or ethylene bridge), 3.71 (t, J=4.6, 4H, morpholinyl), 3.90 (s, 2H, benzylic or ethylene bridge), 7.14 (d,J=2.5, 1H, aryl), 7.37 (d,J=2.5, 1H, aryl), 8.37, (s, 1H, imine), 13.23 (s, broad, 1H, phenolic). ^{13}C: δ 31.28 (CH_3, ^tBu), 33.76 (q, ^tBu), 53.48 (CH_2, morpholinyl), 56.59 (CH_2, Benzylic or ethylene bridge), 59.71 (CH_2, Benzylic or ethylene bridge), 66.88 (CH_2, morpholinyl), 117.67 (q, aryl), 123.95 (q, aryl), 126.76 (q, aryl), 130.93 (CH, aryl), 140.54 (q, aryl), 157.15 (q, aryl), 166.51 (CH, aldehydic). FT-IR: (Dichloromethane film), 736cm^{-1} medium, 803w, 821vw, 863s, 881w, 909w, 1016m, 1032m, 1071m, 1117vs (dialkyl ether a.s. stretch), 1205m, 1281m, 1302m, 1330w, 1394w, 1457 & 1483vs doublet, 1632s, 2853vs, 2959vs (CH stretch).

Synthesis **– N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] 1,3 – Diamino Propane.**

5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde (6.000g, 21.7 mmol) was dissolved in diethyl ether (60ml) and poured into a solution of 1,3 – diamino propane (0.786g, 10.6mmol) in ethanol (60ml). Colour changed instantly to yellow and the solution was stirred overnight. Removing the solvent in vacuo gave the product as a dark yellow oil which was triturated in hexane at –78°C to produce a waxy yellow solid. Washed as above. MP 126-128 °C. Calculated for $C_{35}H_{52}N_4O_4$ – 70.91%C, 8.84%H, 9.45%N, found 70.15%C, 9.05%H, 9.37%N.

FAB-MS m/z, normalised intensity, [assignment]: 594, 621.8% [MH$^+$]; 505, 18.9%, [M$^+$ - morph – 2H]; 422, base peak, [MH$^+$ - 2morph]. NMR ($CDCl_3$) ^{1}H: δ 1.30 (s, 9H, ^{t}Bu), 2.08 (t, J=6.5, 1H, centre propyl methylene), 2.52 (t, J=4.1, 4H, propyl and benzylic), 3.61, (s), and 3.66 (m, J=4.6, 8H, morpholinyl), 7.16 (d, J=2.5, 1H, aryl), 7.40 (d, J=2.5, 1H, aryl), 8.38 (s, 1H, imine), 13.51 (s, broad, 1H, phenolic). ^{13}C δ: 30.80 (CH_3, ^{t}Bu), 31.32 (CH_2, centre propyl methylene), 33.80 (q, ^{t}Bu), 53.49 (CH_2, morpholinyl), 56.57, 56.65 (CH_2, benzylic/propyl), 66.90, (CH_2, morpholinyl), 117.68, 124.04 (q, aryl), 126.55, 130.88 (CH, aryl), 140.52, 157.32 (q, aryl) 165.53 (CH, aldehydic). FT-IR: (Dichloromethane film) 704cm^{-1} very strong, 737vs, 804w, 863s, 884m, 909m, 1007 and 1015 m doublet, 1032w, 1070m, 1116vs (dialkyl ether a.s. stretch), 1206m, 1265vs, 1303w, 1331w, 1363w, 1457w, 1457s, 1483s, 1633s, 2860vs and 2963vs (CH stretch), 3052m, 3940vw, 4195vw.

***Synthesis* – N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] *trans* – 1,2 – diamino cyclohexane.**

5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde (6.000g, 21.7 mmol) was dissolved in diethyl ether (60ml) and poured into a solution of *trans* – 1,2 – diamino cyclohexane (1.210g, 10.6mmol) in ethanol (60ml), resulting in a bright yellow solution. Solvent was removed under vacuum to give product as a yellow oil which could not be triturated. Yield was quantitative. The oil was dissolved in petroleum ether (40-60) and a small amount (1.080g, 1.7mmol) of material crystallised as solvent evaporated, this was collected by filtration. MP 103 – 106 °C. Calculated for $C_{38}H_{56}N_4O_4$ – 72.12%C, 8.92%H, 8.89%N, found 69.19%C, 9.17%H, 8.46%N. FT-IR: (Dichloromethane film) 667w, 702vw, 735m, 805w, 825w, 863s, 880w, 908m, 1017m, 1035w, 1070m, 1117vs (dialkyl ether a.s. stretch), 1205w, 1281m, 1299m, 1331w, 1362m, 1394m, 1456s, 1629s, 2855vs and 2956vs (CH stretch), 3372m, broad (water).

Synth sis – Ethoxy–N–Morpholin-4–yl Methane.

Morpholine (87.12g, 1mole) was added dropwise to a suspension of paraformaldehyde (37.64g, 1.25 mol) and potassium carbonate (276.4g, 2mol) in ethanol (500ml) at 0°C with overhead mechanical stirring. When addition of morpholine was complete, the mixture was

d to warm to room temperature and stirred vigorously for 48 hours. After this time, the solid residues wer filtered off and washed with ethanol (2 × 50ml), filtrate and washings were combiened and concentrated under vacuum to leave a cloudy brown oil. This was distilled through a verigreux column under reduced pressure to give product as a clear, non-viscous liquid. BP 34°C at 0.3 mbar, Yield = 103.12g, 0.71 mol, 71%. Calculated for $C_7H_{15}O_2N$: 57.90%C, 10.41%H, 9.65%N, Found: 55.10%C, 10.37%H, 10.35%N, (analyst's comments: "Evaporating too quickly, used an Al capsule, therefore expect N values to be a bit high".) EI-MS: 100m/z, base peak, $[O(CH_2CH_2)_2NCH_2^+]$, no M^+ peak observed.

Synthesis –5-nonyl-Salicylaldehyde.

Magnesium methoxide catalyst was generated in situ by refluxing magnesium raspings (7.3g, 0.3 mol) and magnesium methoxide (1.75g of 7.4% w/w methanolic solution, 1.5 mmol) in methanol (##ml) and toluene (##ml) for 2 hours. When all the magnesium was dissolved and H_2 evolution had ceased 4-Nonyl phenol (112g, 0.5mol) was added and mixture was refluxed for a further hour. Toluene was added and the methanol –toluene azeotrope was removed by distilation at 85°C. A slurry of paraformaldehyde (45g, 1.5mol) in toluene was added to reaction over 50 minutes with concurrent removal of the volatile products by distillation. Stirring was continued at 95 – 100°C for 2 hours, then the mixture was cooled to room temperature. Solvent was removed under reduced pressure yielding the product as a pale yellow oil, purified by short path distillation under vacuum. B.P at 120°C at 1.0 mbar. NMR ($CDCl_3$) ^1H: δ 0.46 – 1.77 (m, J=1.2 – 6.4, 19H nonyl), 6.82 (d, J=9.2, 1H, aryl *ortho* to aldehyde), 7.45 (m J=7-9, 2H, aryl, *meta/para* to aldehyde), 9.88 (s, 1H, phenolic), 10.87 (s, 1H, aldehydic). ^{13}C δ:8.36 – 52.21 (96 peaks, nonyl), 116.94 (CH aryl), 119.90 (q, aryl), 130.42 (CH aryl), 135.42 (CH aryl) 159.22 (q, aryl), 196.81 (CH, aldehydic). FT-IR (NaCl plates, no nujol): 741w, 775w, 834w, 1167 and 1181 weak doublet, 1214 and 1231 w doublet, 1283s, 1378m, 1484s, 1589w, 1654vs (Carbonyl stretch), 2928s and 2960vs (CH stretch). EI-MS: 248, 10%, $[M^+]$, 233, 3%, $[M^+ - CH_3]$, 219, 12%, $[M^+ - CH_3 – CH_2]$, 205, 8%, $[M^+ - CH_3 – 2CH_2]$, 191, 15%, $[M^+ - CH_3 – 3CH_2]$, 177, 38%, $[M^+ - CH_3 – 4CH_2]$, 163, 100%, $[M^+ - CH_3 – 5CH_2]$,

149, 42, [M^+ - CH_3 – $6CH_2$], 135, 35%,[M^+ - CH_3 – $7CH_2$], 121, 7%, [M^+ - CH_3 – $8CH_2$]. Calculated for $C_{16}H_{24}O_2$: 77.37%C, 9.74%H. Found: 77.54%C, 10.05%H.

Synthesis – 5-nonyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

Ethoxy-N-morpholin-4-yl methane (15.95g, 0.11mol) and 5-nonyl-Salicylaldehyde (24.8g, 0.1mol) were placed in a 500ml three-necked round bottomed flask and dissolved in acetonitrile (150ml). This solution was heated under reflux in an N_2 atmosphere for 66 hours, after which time solvent was removed under reduced pressure to yoeld product as a brown oil. Thin layer chromatography (1% methanol in chloroform) revealed that some unreacted aldehyde remained. Purification was attempted by dry flash chromatography on a silica column eluted with chloroform, with an increasing methanol content gradually increasing the polarity. This was only partially successful because the amount of material too much for the size of column used – product fractions were collected and concentrated in vacuo but TLC revealed product still retained a small quantity of unreacted aldehyde. Crude yield = 34.9g, 0.10043mol, 100.43% ! impure product. NMR ($CDCl_3$) ^1H δ: 0.42 – 1.70 (m, 22H, should be 19 from nonyl), 2.54 (s, 4H, morpholinyl), 3.68 (s) and 3.74 (t, J=4.6) 6H, morpholine and benzylic overlapping, 7.35 and 7.51 (m, J=2.4, 2H, aryl), 10.62 (m, J=2.3, 1H, aldehyde? Should be a singlet), phenolic resonance absent due to exchange with deuterated solvent. Calculated for $C_{21}H_{33}NO_3$: 72.57%C, 9.57%H, 4.03%N. Found: 70.98%C, 9.48%H, 3.44%N. FT-IR: 610w,667w, 755vs, 801m, 835vw, 864vs, 909s, 969m, 1001m, 1019m, 1071m, 1118vs (dialkyl ether a.s. stretch), 1285s broad, 1381s, 1455vs broad, 1605s, 1651vs,1682vs, 2958vs broad (CH stretch). EI-MS: 347, 25.7% [M^+], 319, 28.6%, [M^+ - CO], 304, 10.9% [M^+ - CO – CH_3], 290, 21.8%, [M^+ - CO – CH_3 – CH_2], 276, 27.2% [M^+ - CO – CH_3 – $2CH_2$], 262, 35.9% [M^+ - CO – CH_3 – $3CH_2$], 248, 21.2%, [M^+ - CO – CH_3 – $4CH_2$], 234. 14.3%, [M^+ - CO – CH_3 – $5CH_2$], 219, 21.6%[M^+ - CO – $2CH_3$ – $5CH_2$], 205, 24.2%, [M^+ - CO – $2CH_3$ – $6CH_2$], 191, 35.4%, [M^+ - CO – $2CH_3$ – $7CH_2$]; 86, base peak, [$O(CH_2CH_2)_2N^+$]. This EI-MS spectrum suggests the major componant of the mixed isomer nonyl side chain has a methyl branch at the 3rd carbon.

Synthesis – 5-tert-Butyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

Ethoxy-N-morpholinyl methane (15.95g, 0.11mol) and %-tert-Butyl Salicylaldehyde (14.8g 0.1mol) were dissolved in acetonitrile (150ml) and heated under reflux in an N_2 atmosphere for 24 hours. Thin layer chromatography (1% methanol in chloroform) revealed residual aldehyde but almost no morpholinyl methane in the reaction mixture, so extra morpholinyl methane (16.00g 0.11mol) was added and the mixture refluxed for a further 66 hours. TLC indicated that all the aldehyde had reacted, solvent was removed on a rotary evaporator yielding crude product as a pale green oil. Yield 39.427g, 140% suggesting that some acetonitrile remains in the oil. Mixture was dissolved in dichloromethane (150ml), washed with water (3 x 60ml) and conetrated in vacuo. NMR ($CDCl_3$) ^1H δ: 1.28 (s,9H, nonyl), 2.55 (m, J=4.6, 6H? expect 2H benzylic), 3.69 (m, J=2.1, 8.5H, morpholinyl), 7.03 (s) 7.37 (d, J=2.6) and 7.59 (d, J=2.6) (2H, aryl), 10.23 (s, 0.5H, aldehyde), phenolic resonance absent due to exchange. ^{13}C δ:31.16 (CH_3, ^tBu), 33.96 (q, ^tBu), 52.99 (CH_2, morpholinyl), 59.34 (CH_2, benzylic), 66.65 (CH_2, morpholinyl), 81.53 (q, aryl), 88.34 (q, aryl), 125.63 (CH aryl), 133.41 (CH aryl), 133.41 and 158.60 (q, aryl), 192.59 (CH, aldehydic). Calculated for $C_{16}H_{23}NO_3$: #%C, #%H, #%N. Found: #%C, #%H, #%N. FT-IR: 736w, 864m, 1118vs (dialkyl ether a.s. stretch), 1616m, 1269m, 1298vw, 1364vw, 1396vw, 1457s, 1481s, 1606m, 1653m, 1681s (carbonyl stretch), 2854s and 2960s (CH stretch). FAB-MS: (Matrix: THIO) 422, 3.6%, [M^+ + ^tBu + morph + 2H], 337, 3.2%, M^+ + ^tBu + 3H], 278, 16.9% [M^+], 262, 25.8%, [M^+ - OH_2], 191, 45.4% [M^+ - morph], where ^tBu = $(CH_3)_3C^*$, morph = $O(CH_2CH_2)_2N^*$.

***Synthesis* – N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine Nickel Sulfate complex.**

5-tert-Butyl-3-(morpholin-4-yl methyl) Salicylaldehyde (0.50g,).86mmol) was dissolved in methanol (30ml) and add d to a hot solution of nickel sulfate heptahydrate (0.245g, 0.86mmol) in methanol (20ml), instantly producing a dark orange colour. Removing the solvent under

reduced pressure gave the product as an amorphous solid, triturated in ether to form deep red crystals which turned orange when ground to a powder. Yield 590mg, 93.6%.Material soluble in polar organic solvents. $\chi_m = 1.14 \times 10^{-9}$, $\mu_{eff} = 0$. Evaporating methanol from a dilute solution in a 100ml conical flask produced X-ray diffraction grade single crystals. NMR was paramagnetically broadened, indicating some difference between solid and solution state structure. FAB – MS: 798, 2.3%, [?], 733, 10.1%, [ligand + Ni + SO_4], 635, 72.4% [Ligand + Ni], 549, 1.2% [ligand + Ni – morph], 479, 5.7% [?], 463, 100, [ligand + Ni – 2morph].

Synthesis **– N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine Nickel Nitrate complex.**

Nickel Nitrate hexahydrate (99mg, 0.34mmol) was dissolved in hot methanol (20ml) and added to a hot solution of dimorphylSALEN (200mg,0.34mmol) in methanol (30ml). A red orange colour formed instantaneously on mixing. The methanol was removed in vacuo leaving a glassy red-orange solid, which was crystallised in diethyl ether and recovered by filtration, yield = 253mg, 0.33 mmol, 97.8%. $\chi_m = 2.11 \times 10^{-10}$, $\mu_{eff} = 0$. NMR is paramagnetically broadened. FAB – MS: 783, 5.4% [?], 699, 1.6%, [ligand + Ni + NO_3], 698, 4.0%, [ligandH^+ + Ni + NO_3], 635, 100, [ligand + Ni], 550, 5.3% [ligand + Ni - morph], 463, 97.3% [ligand + Ni – 2morph]. Dissolving the material in dichloromethane and layering with hexane produced XRD grade single crystals.

Synthesis **– N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine Nickel Acetate complex.**

Nickel Acetate tetrahydrate (85mg, 0.34mmol) was dissolved in hot methanol (20ml) and added to a hot solution of dimorphylSALEN (200mg,0.34mmol) in methanol (30ml). Mixture instantly turned red-orange. The methanol was removed in vacuo leaving a glassy red-orange solid, which was crystallised in diethyl ether and recovered by filtration, yield = 167mg, ##mmol ##%. MP ## °C. $\chi_m = 2.47 \times 10^{-10}$, $\mu_{eff} = 0$. NMR is paramagnetically broadened. FAB

ing hexane vapours into an ethyl acetate solution of the complex grew single crystals suitable for X-ray structure determination.

***Synthesis* – N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane Nickel Sulphate complex.**

Nickel Sulfate heptahydrate (104mg, 0.37mmol) was dissolved in hot methanol (20ml) and added to a hot solution of N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (200mg,0.37mmol) in methanol (30ml). Mixture instantly turned brown. 20ml of solution was removed and concentrated in vacuo leaving a glassy brown solid, the remainder was left to stand in a sealed conical flask. The solid was crystallised in ether and recovered by filtration, yield = 95mg. Assuming sample is representative of whole solution, yield = 238mg, 0.32mmol, 86%.

***Synthesis* – N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane Nickel Nitrate complex.**

Nickel Nitrate hexahydrate (85mg, 0.37mmol) in methanol (20ml) was added to a hot solution of N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (200mg,0.37mmol) in methanol (30ml), changing colour to brown. After stirring for ca. 5 minutes, 15ml solution was removed and concentrated invacuo and the rest was put aside to stand in a sealed conical flask. Removing the solution gave a brown amorphous solid whch was crystalised in ether and recovered by filtration.

Synthesis – 5-Methyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

5-Methylyl Salicylaldehyde (27.85g, 0,205 mol) and Ethoxy-N-morpholinyl methane (30.45g, 0.210mol) were refluxed together in acetonitrile (150ml) under an N_2 atmosphere for 48 hours. Reaction mixture was cooled to room temperature and concentrated in vacuo leaving a green oil. This was dissolved in HCl (2M, 100ml) and extracted in ether (3×80ml). Aqueous was then basified to pH 9 with 1M KOH, forming a yellow precipitate and a green oil. Yield 36.559g, 0.155mol, 75.8%. Calculated for $C_{13}H_{17}NO_3$: 66.36%C, 7.28%H, 5.95%N, Found: 65.86%C,

7.80%H, 6.82%N. EI-MS: 306, 1.3% [M$^+$ + 2CO + CH_3], 235, 27.9% [M$^+$], 219, 3.2% [M$^+$ - O] 207, 82.9%, [M$^+$ - CO], 188, 3.7% [], 177, 8.3%, [], 162, 5.7%, [], 149, 25.3%[M$^+$ - morph], 120, 8.9%, [M$^+$ - morph - CHO], 86, 100%, [morph]. FT-IR: 617m, 804m, 863vs, 909s, 953m, 994s, 1031m, 1071m, 1116vs (ether a.s. stretch), 1260vs, 1456 and 1472 vs doublet, 1498s, 1606vs, 1652vs (carbonyl stretch?), 1682vs 2339 and 2359 w doublet, 2731w (aldehye CH stretch), 2852vs and 2960vs broad (CH stretch).

Synthesis – 5-Nonyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

Ethoxy-N-morpholinyl methane (15.95g, 0.11mol) and 5-Nonyl-Salicylaldehyde (24.8g, 0.1mol) were placed in a 500ml three neck RB flask and refluxed in acetonitrile (200ml) under and N_2 atmosphere for 66 hours. TLC (1% methanol in chloroform) indicated that although some morpholine remained, all the aldehyde had reacted. (Morpholine r_f=0.102, product r_f=0.792.) The product was concentrated in vacuo to give a yellow oil. Attempts to purify by dry flash chromatography on a silica column proved unsuccessful because there was too much material for the size of column used. Crude yield = 34.90g, 0.10057mol, 100.57% indicating product contains some residual solvent and unreacted ethoxy-N-morpholinyl methane.

***Synthesis* – N,N' - bis [5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine.**

5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (2.824g, 8.13mmol) was dissolved in diethyl ether (30ml) and poured into a solution of ethylene diamine (0.243g, 4.05mmol) in ethanol (30ml). The colour instantly changed to yellow and after stirring overnight the resulting solution was concentrated in vacuo to give crude product as a yellow oil.

***Synthesis* – N,N' - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane.**

5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (3.30g, 9.50mmol) was dissolved in diethyl ether (30ml) and poured into a solution of diamino propane (0.348g, 4.70mmol) in thanol

(30ml), forming a yellow solution. Removing soluvent in vacuo gave crude product as a yellow oil.

***Synthesis* – N,N' - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] *trans* – 1,2 – diamino cyclohexane.**

5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (2.92g, 8.40mmol) was dissolved in diethyl ether (30ml) and poured into a solution of *trans* – 1,2 – diamino cyclohexane (0.474g, 4.15mmol) in ethanol (30ml) to form a yellow solution. This was concentrated in vacuo to give the crude product as a yellow oil. $C_{48}H_{76}N_4O_4$

***Synthesis* – N,N' - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] *ortho* – Phenylene diamine.**

Ortho – phenylene diamine (0.422g, 3.90mmol) as dissolved in ethanol (30ml) in a flask covered in tin foil to protect from light. This was added to a solution of 5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (2.75g, 7.92mmol) in diethyl ether (30ml) and stirred overnight, again in the dark. Resulting brown solution was concentrated in vacuo to give the crude product as a dark brown oil. Calculated for $C_{48}H_{70}N_4O_4$ – 75.16%C, 9.20%H, 7.31%N, found 74.52%C, 10.08%H, 5.88%N. NMR ($CDCl_3$) ^1H: δ ^{13}C: δ FT-IR: (Thin film in NaCl plates). Crude yield after evaporation = 3.438g, 4.48mmol, 115% oil obviously retaining some solvent.

Solvent Extraction with N,N' - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] *ortho* – Phenylene diamine.

N,N' - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] *ortho* – Phenylene diamine (0.7710g, 1.0mmol) was dissolved in toluene (10ml) to make a 0.1 M solution. 5ml of this was placed in a sealed jar with aqueous nickel sulfate solution (7.5ml, 0.5M) and stirred overnight. The experiment was replicated exactly except the aqueous solution was adjusted to pH 1.8 by the addition of conc. HCl. After the two phases had stirred together for 24hours, the toluene solution had turned pale brown and a very viscous dark brown third phase had formed in both experiments, especially in the pH 1.8 system. 1 ml of organic was removed and evaporated to

dryness. The solid residues were dissolved in boiling aqua regia (ca. 15ml) and diluted with ca 40ml of deionised water. A small amount of waxy precipitate formed upon dilution, so the solution was filtered through glass wool, the residues were washed with water and the solution and washings were combined in a graduate flask and made up to 100ml. A further 0.5 ml of the loaded organic solution was removed and diluted up to 100ml with Stoddard's solvent.

The experiment was repeated as above using chloroform in place of toluene. There was no evidence of a viscous third phase appearing in the system, the loaded chloroform solution was insoluble in Stoddard's solvent.

***Synthesis* – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] *ortho* – Phenylene diamine.**

Ortho – phenylene diamine (2.163g, 20mmol) was disolved in ethanol (150ml). The flask was wrapped in tin fiol to protect the materiaml from light. This was added to a solution of 5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde (10.86g, 39.2mmol) in ether (150ml), again in the dark. After stirring for ca. 10 minutes the solution was concentrated in vacuo to leave a dark brown oil, crude yield = 11.36g, 18.4mmol, 93%. This was dissolved in hexane/ether 2:1 (ca 300ml). A small amount of brown solid remained undissolved and was removed by filtration. The solvent was allowed to evaporate slowly from a 500ml conical flask to leave a semi-crystalline orange material. This was dried under vacuum (oil pump) for 18 hours. Yield = 10.07g, 16.1mmol, 83.8%. FAB-MS 627, 8.5%, [MH$^+$], 531, 3.0%[], 511, 13.6%, [MH$^+$ - 2^{t}Bu], 422, 44.1 %, [], 368, 70.3%, []. FT-IR (NaCl plates): 743m, 803w, 863m, 880w, 909w, 1005w, 1017vw, 1038w, 1070w, 1117vs (dialkyl ether a.s stretch), 1192vw, 1205vw, 1270vw, 1300w, 1362w, 1394w, 1456m, 1482m, 1494m, 1590m, 1616m (conjugated imine), 2856s and 2959vs (CH stretch), 3361s, broad, (water {phenol?}). NMR ($CDCl_3$), ^{1}H δ: (looks a bit untidy) 1.18-1.34 (m, J=8 and J=12, 9H, ^{t}Bu), 2.46 – 2.57 (m, J=4.6, 4H, morpholine), 3.62-3.76 (m, J=7.0, 8H ? morph + benzylic should be 6H), 6.68 – 7.43 (3m's, J= 1.4, 1.2, 2.0, 4H, aryl), 8.67 (s, ½H, imine). Phenolic resonance missing due to exchange with $CDCl_3$.

***Synthesis* – N,N' - bis [5-*tert*-Butyl-3-(m rpholin-4-yl methyl) salicilaldehyde] *Ortho*-Phenylene diamine Nickel Sulfate complex.**

A small amount of ligand (037g, 0.6mmol) was dissolved in methanol and stirred up with stoichiometric amount of nickel sulfate (1669mg, 0.6mol) forming a red brown solution. The solvent was removed in vacuo leaving a brittle red brown glass This was ground to a powder and found to be soluble in polar and chlorinated solvents, sparingly soluble in toluene and insoluble in hexane.

Solvent Extraction with N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] *ortho* – Phenylene diamine.

N,N' - bis [5-*tert*-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] *ortho* – Phenylene diamine (0.3134g, 5mmol) was dissolved in dichloromethane (10ml) to make a 0.05M solution. 5ml of this was stirred overnight with aqueous nickel sulfate (5ml, 0.5M). Three of these experiments were performed with the aqueous feed pH adjusted to 2.00, 3.5 and 4.68 with sulphuric acid. It was found that the organic solution had turned dark brown but the two phases were very slow to disengage with some of the brown colouration (and presumably the extracant-nickel sulphate complex) partitioned to the aqueous. 0.25ml of the dichloromethane solution was removed and diluted up to 25ml with Stoddard's solvent for ICP-AES analysis.

The experiment was repeated as above using chloroform in place of dichloromethane, with the $NiSO_4$ solution pH adjusted to 0.87, 1.28, 2.50, 3.01, 3.76, 4.10. 5.19 and 5.38 by addition of sulphuric acid or aqueous ammonia. 0.25ml of chloroform solution was removed from each extraction experiment and diluted up to 25 ml with Stoddard's solvent, except for those loaded from pH 0.87, 2.50 and 3.01; these were insoluble in Soddard and m-xylene was used instead. The chloroform solution from pH 1.28 was insoluble in Xylene or Stoddards, so 0.25 ml was evaporated to dryness and the solid residues were dissolved in aqua regia (5ml) and diluted up to 25ml with deionised water.

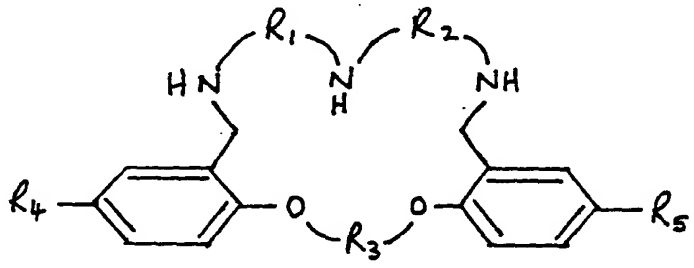
CLAIMS

1. A method of removing both the cation(s) and the anion(s) of a metal salt from an aqueous medium, by means of a ligand having binding sites for both the cation(s) and the anion(s).

2. A method according to claim 1, wherein the ligand has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, the method involving the steps of: adding a said water-immiscible extraction medium to said aqueous medium, whereby said ligand with said cation(s) and said anion(s) bound thereto is partitioned preferentially in a water-immiscible phase; and separating said water-immiscible phase with said ligand-bound cation(s) and anion(s) therein from said aqueous medium.

3. A method according to claim 1, wherein the ligand is immobilised on a solid support.

4. A method according to any of claims 1 to 3, wherein the ligand is of the following formula:



where R_1, R_2 and R_3 are, independently, substituted C_2 to C_4 linkages;

R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

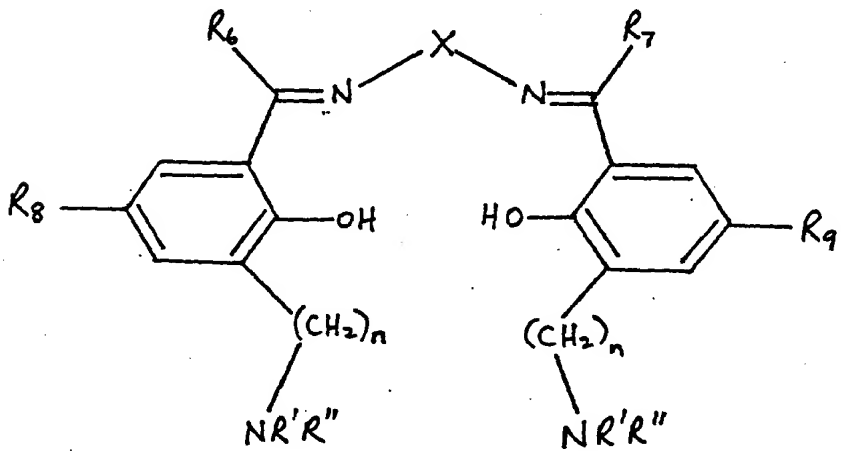
5. A method according to claim 4, comprising the further steps of: contacting the ligand-bound salt with an aqueous ammoniacal solution to produce an aqueous ammoniacal solution of the metal salt; and electrolysing said solution to produce elemental metal and an ammonium salt.

6. A method according to any of claims 1 to 3, wherein the cation binding site of the ligand comprises at least one coordinating acid group, and the anion binding site comprises at least one protonatable base.

7. A method according to claim 6, comprising the further steps of: contacting the ligand-bound salt with a strong acid to protonate the ligand and release the metal cation(s); and electrolysing the resulting solution to product elemental metal.

8. A method according to claim 7, comprising the further steps of contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

9. A ligand suitable for carrying out the method of any of claims 6 to 8, of the following formula:



where: X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

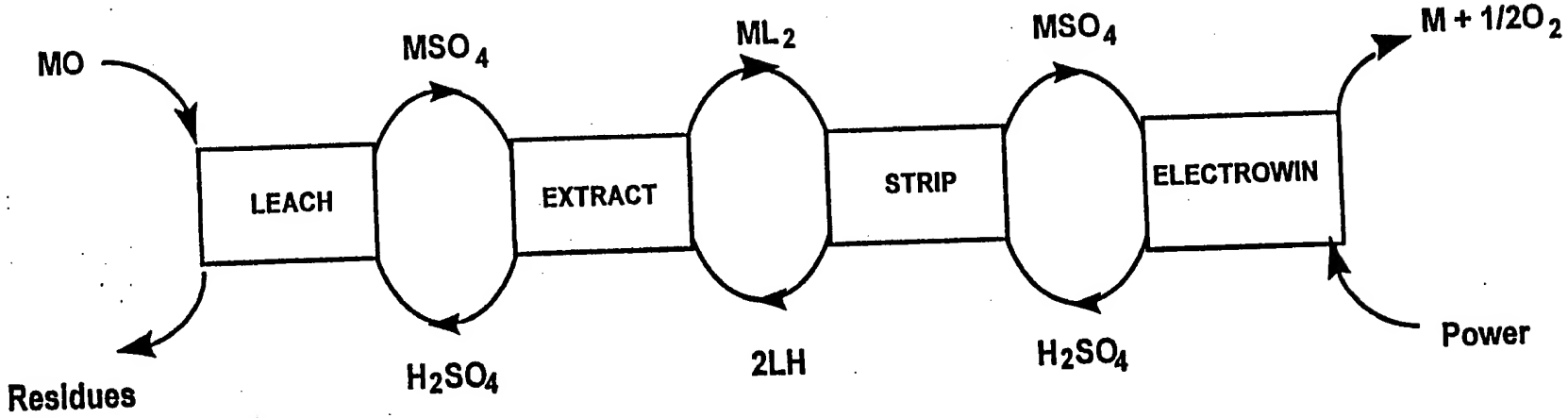
n = 2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

NR'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring.

10. A ligand according to claim 9, wherein NR'R" is a morpholine ring.

FIG 1
(PRIOR ART)



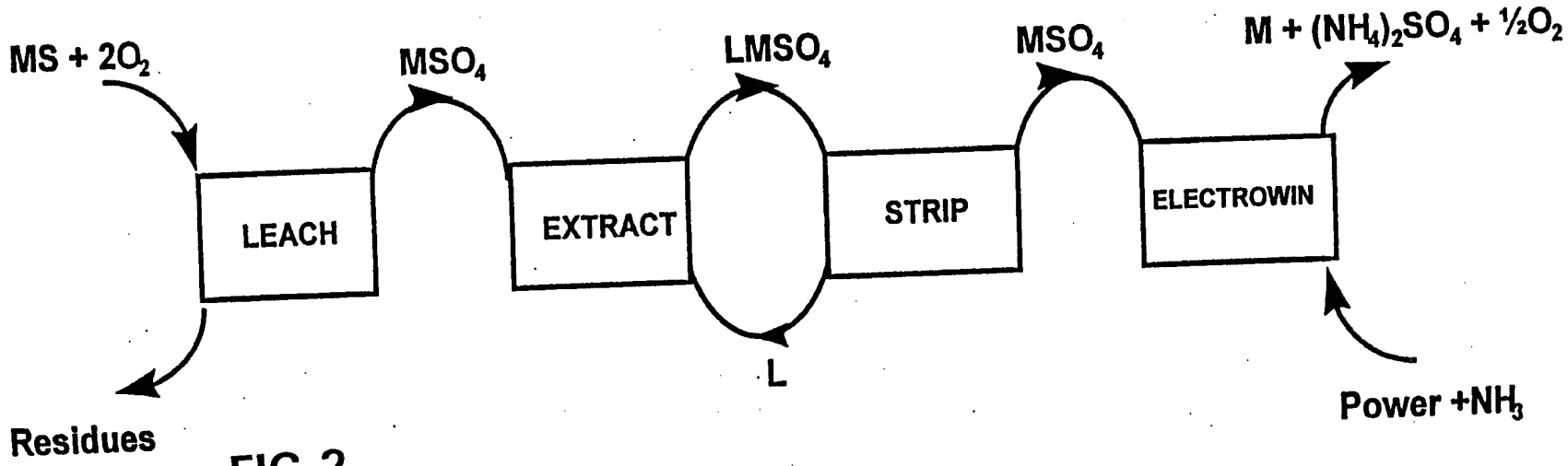
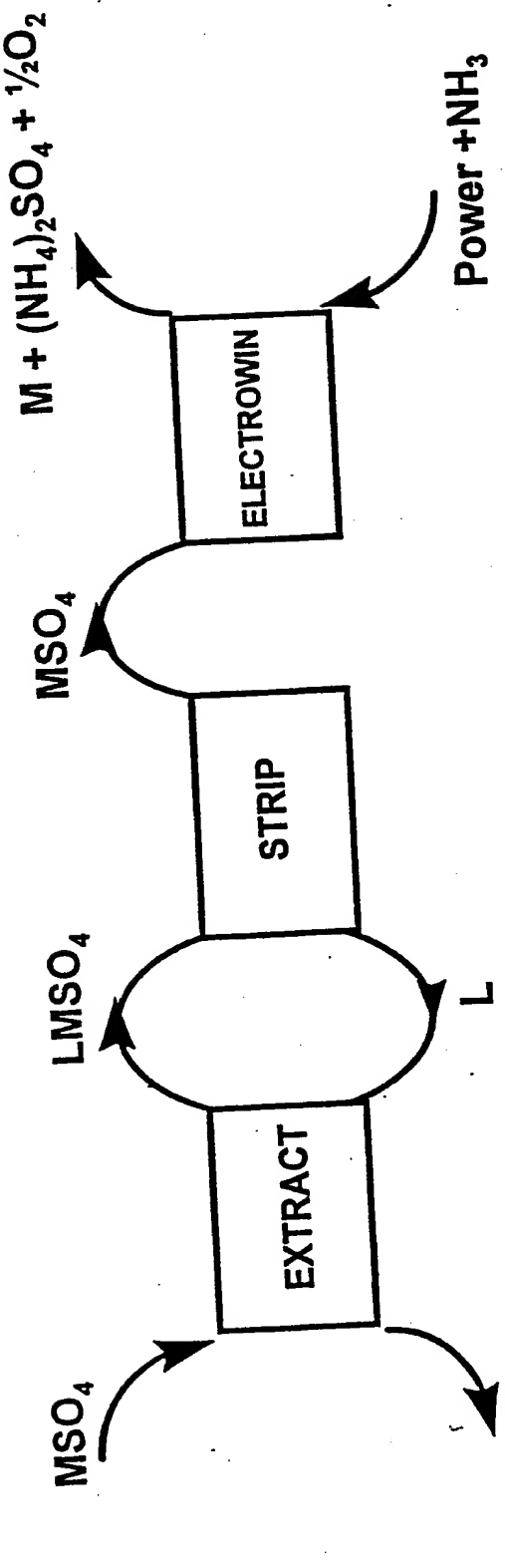


FIG 2


M + $(NH_4)_2SO_4$ + ½O_2
Power +NH_3
ELECTROWIN
MSO_4
STRIP
$LMSO_4$
L
EXTRACT
MSO_4
Purified Stream

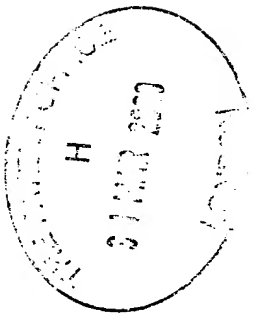



FIG 3